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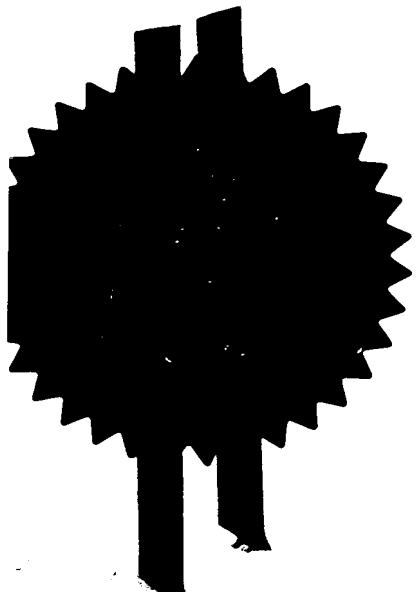
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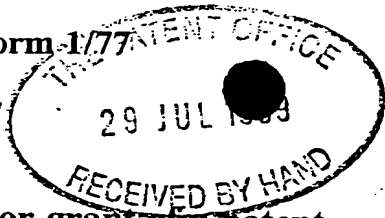
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Patents ADP number <i>(if you know it)</i>	C951438001		
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4. Title of the invention	Process		
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Description 34

Claim(s) 5

Abstract -

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11. I/We request the grant of a patent on the basis of this application.

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Date 29 July 1999

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Process

The present invention relates to a process for the preparation of olefin polymers (e.g. olefin copolymers), in particular to a process for the preparation of copolymers of ethylene or propylene with α -olefins, having a controlled comonomer incorporation across their molecular weight distribution.

The molecular weight distribution (MWD) of a polymer affects its properties, in particular its mechanical strength and processing properties. Mechanical strength is to a large extent determined by the high molecular weight fraction, whereas extrudability is determined by the low molecular weight fraction. As a result, polyolefins having improved mechanical and processing properties can be obtained if the molecular weight distribution is tailored to the end use of the polymer. For many applications, such as extrusion and molding processes, polymers having a broad, or multi-modal, molecular weight distribution are desirable. Polymers having a multi-modal MWD consist of two or more polymer components and are generally characterised by a broad MWD. Such polymers exhibit excellent processability.

The mechanical properties of polymer products can be further manipulated by the inclusion of α -olefin comonomers, for example by varying the nature and relative content of the side chains (or short chain branches) which may be introduced. Depending on the nature of the comonomer, its inclusion may result in an increase or a decrease in the degree of branching on the main polymer backbone. Typically, inclusion of comonomer will result in an increase in the relative content of side chains.

Not only the nature, but also the distribution of any side chains among the individual polymer components

is important in determining the polymer properties. The ability to control the comonomer distribution over the MWD of the polymer is therefore particularly desirable, in particular the ability to produce multi-modal, e.g. bi-modal, MWD copolymers in which comonomer is selectively incorporated in one part of the molecular weight distribution. Polymers having a multi-modal, e.g. bi-modal, MWD in which comonomer is concentrated in a higher molecular weight fraction are especially desirable, in particular those polymers in which inclusion of comonomer in a high molecular weight fraction results in an increase in the relative content of side chains. Such polymers exhibit good impact resistance, tear strength, and environmental stress crack resistance (ESCR). Although not wishing to be bound by theory, it is believed that the presence of a polymer chain defect, such as a comonomer, in a high molecular weight fraction of the polymer could stimulate formation or enhance the effect of "tie molecules" which are able to participate in more than one crystal lamella. This is believed to contribute to the improved mechanical, especially improved ESCR properties, of the resulting polymer.

In an attempt to achieve improved ESCR properties at corresponding MFR and densities, several suggestions have been made to blend low molecular weight homopolymer and high molecular weight copolymers, for example by reactor blending (reactors in series) or by blending the two separate components in an extruder (see e.g. US-A-3280220, US-A-4461873 and US-A-4547551). However, it can be difficult to mix polymers with different molecular weights to achieve a homogeneous product. In order to get uniform, homogeneous blends from two widely different molecular weight polymers, it is generally necessary that at least 50% by weight of the blend be of the high molecular weight component. Homogeneous blends having > 50% by weight of the low molecular weight

component are extremely difficult to obtain by blending methods.

Various catalyst systems have been proposed for the polymerization of polymers and copolymers of olefins. Typically, these involve sequential polymerization in multiple reactors operating at different conditions which, although providing versatility in terms of the properties of the final polymer product, can be inefficient. Polymer preparation carried out in a single reactor under essentially constant polymerization conditions is more economical and therefore desirable.

The preparation of broad MWD olefin polymers in a dual reactor system using a variety of transition metal catalysts, e.g. Ziegler catalysts, is described for example in NO-923334. The broad MWD results in this case from the polymerization conditions in the different reactors favouring the production of different molecular weight polymers, e.g. one favouring the production of a higher molecular weight polymer and a second favouring production of a lower molecular weight polymer.

Broad MWD polyolefins can be produced in a single reactor using either catalyst mixtures or multi-site catalysts, e.g. two or more metallocene complex catalysts. For example, WO 95/04761 describes the use of a combination of three metallocene complexes to produce a polymer product having a controlled molecular weight distribution. However, such a catalyst system provides for little control over the levels of comonomer incorporation.

Both conventional Ziegler-Natta and Phillips type catalysts, e.g. chromium oxide based catalysts, have been proposed for use in combination with metallocenes in the preparation of ethylene copolymers having a bimodal, or broad, molecular weight distribution (see e.g. EP-A-676418, EP-A-658571, US-A-5543376, US-A-5624877 and WO97/27225). However, both Ziegler and Phillips type catalysts have a tendency to produce polymer products

having an inverse dependence of molecular weight and comonomer content, i.e. the lower molecular weight polymer molecules contain a relatively higher proportion of comonomer than the higher molecular weight polymer molecules. Thus, although a degree of comonomer control is achieved, this is generally limited to incorporation of comonomer in a lower molecular weight component. As a result, the polymer products exhibit a relatively poor balance of impact and stiffness and low ESCR.

There thus exists the need for a process for the preparation of copolymers which provides for a greater degree of control over the level of comonomer incorporation, in particular a process capable of producing polymer products in which the degree of comonomer incorporation in a higher molecular weight fraction is greater than that in a lower molecular weight fraction. Most especially, there is a need for such a process which may be performed in a single reactor, preferably a process in which conditions in the reactor vessel (e.g. temperature, pressure, comonomer and hydrogen concentration, etc.) remain essentially constant during polymerization.

We have now found that copolymers having a tailored MWD in combination with controlled inclusion of α -olefin comonomers, in particular copolymers in which comonomer is concentrated in a higher molecular weight fraction, can be produced if polymerization is effected in the presence of a multi-site, preferably a dual-site, catalyst having catalytic sites with different propensities for incorporating comonomer. Particularly surprisingly, we have found that intimate mixes of polymers having very different levels of comonomer incorporation may be achieved using catalysts selected from a single family of catalysts. Advantageously, such a process may comprise a single polymerization stage and can be performed in a single reactor.

Thus, viewed from one aspect the invention provides

a process for the preparation of an olefin copolymer, wherein olefin polymerization is effected, preferably in a single reactor section, in the presence of an olefin polymerization catalyst having catalytic sites with different propensities for comonomer incorporation. Preferably at least 20 to 60 wt%, most preferably at least 90 wt% of the polymer, e.g. 100 wt% of the polymer, is prepared in a single polymerization stage or single reactor section, i.e. under substantially constant process conditions (not varying significantly with time).

Conveniently, the process of the invention is effected in the presence of an olefin polymerization multi-site catalyst, e.g. a dual-site catalyst, capable of producing polymers, preferably multi-modal (e.g. bi-modal) molecular weight distribution polymers, comprising at least first and second polymer components having different levels of comonomer incorporation. Preferably, the catalyst used in the process of the invention is one capable of producing under polymerization conditions substantially constant with time, polymers in which the comonomer content of a first polymer component is at least 3, preferably at least 5, e.g. at least 10, times higher than that of a second polymer component. Most preferably, the catalyst for use in the invention is one capable of producing a polymer in which the comonomer content of a higher molecular weight component of the polymer is at least 3, preferably at least 5, e.g. at least 10, times the comonomer content of a lower molecular weight component. The level of comonomer incorporation in one or more, e.g. in one component of the polymer, typically in a lower molecular weight component of the polymer, may be zero or substantially zero in which case the latter may be a homopolymer, e.g. an ethylene homopolymer. Especially preferably, the catalyst is one capable of producing a polymer in which short chain branching is

mainly, e.g. exclusively, present in a higher molecular weight component. Incorporation of short chain branches in the higher molecular weight chains is believed to enable incorporation of higher levels of comonomer into the polymer at constant density. This in turn helps to achieve a high ESCR.

Viewed from a further aspect the invention provides an olefin copolymer obtainable by the process in accordance with the invention, and products (e.g. containers, fibres, films, sheets, tubes, etc.) fabricated therefrom. Polymers produced by the process are preferably homogeneous and this forms a further aspect of the invention.

Viewed from another aspect the invention provides a multi-site polymerization catalyst, preferably a dual-site catalyst, in particular an olefin polymerization catalyst, having catalytic sites capable of producing under essentially constant polymerization conditions, polymers, preferably multi-modal (e.g. bi-modal) molecular weight distribution polymers, comprising at least first and second polymer components having different levels of comonomer incorporation. Preferably, the levels of comonomer incorporation in the first and second polymer components will differ by a factor of at least 3, preferably at least 5, e.g. at least 10. Most preferably, the catalytic site capable of producing a higher molecular weight component of the polymer is capable of a higher level of comonomer incorporation.

Preferred catalysts for use in the process of the invention are those having catalytic sites capable of producing polymer components having a weight average molecular weight (Mw) in the range 1,000 to 10,000,000, preferably 2,000 to 1,000,000, e.g. 2,000 to 500,000. Especially preferred catalysts are those having a first catalytic site capable of producing a relatively lower Mw (higher MFR) polymer (e.g. having a weight average

molecular weight in the range 1,000 to 1,000,000, preferably 2,000 to 500,000) with a lower level of comonomer incorporation, and a second catalytic site capable of producing a relatively higher Mw (lower MFR) polymer (e.g. having a weight average molecular weight in the range 10,000 to 10,000,000, preferably 50,000 to 1,000,000) with a higher level of comonomer incorporation. Typical levels of comonomer incorporation in a lower molecular weight component of the polymer are in the range 0 to 50, e.g. 0 to 25. Typical levels of comonomer incorporation in a higher molecular weight component of the polymer will be in the range from 0.1 to about 333, e.g. 5 to 100.

As used herein, the terms "comonomer level", "level of comonomer incorporation" and "comonomer content" are used interchangeably and are intended to define the average comonomer content of any given polymer component over its entire molecular weight range. Typically, comonomer level is determined by the short chain branching frequency (SCBF), i.e. the number of short chain branches per thousand carbon atoms (SCB/1000 C atoms). This may be illustrated in the case of a homopolymer of propylene in which a single monomeric unit comprises two backbone carbon atoms and one branching (methyl) group, i.e. $\frac{1}{3}$ branch per carbon atom. This corresponds to a comonomer level (branches per 1000 C atoms) of $1000/3$.

However, comonomer level need not be determined by the number of short chain branches per thousand carbon atoms. For example, in the case of polymers consisting mainly of branched polymer units, e.g. polypropylene, the comonomer to be incorporated may include non-branched or linear comonomers such as ethylene. Comonomers which serve to reduce the degree of branching may act as crystallinity-disrupting units which result in a decrease in the crystallinity of the polymer material. In such cases, the comonomer level is

determined by the average number of non-branched (or linear) units per thousand carbon atoms.

The process of the invention is for the polymerization of olefins, preferably a mixture of olefins, in particular α -olefins, e.g. C_{2-10} α -olefins. The polymer product will be a copolymer (which term is used herein to include polymers deriving from two or more monomer species). Preferably at least 50% by weight of the polymer derives from a C_{2-10} α -olefin monomer, more particularly from a C_{2-4} α -olefin monomer, preferably ethylene or propylene. The other monomer(s) may be any monomers capable of copolymerization with the olefin monomer, preferably mono or polyunsaturated C_{2-20} compounds, in particular monoenes or dienes; especially C_{2-10} α -olefins such as ethene, propene, but-1-ene, pent-1-ene, hex-1-ene, oct-1-ene or mixtures thereof. Bulky comonomers, e.g. styrene or norbornene may also be used.

The process is particularly effective for the preparation of copolymers of ethene with one or more copolymerizable monomers, e.g. C_{3-20} mono and dienes, more preferably C_{3-10} α -olefin monomers, and for the preparation of copolymers of propene with one or more copolymerizable monomers, e.g. C_{4-20} mono and dienes, more preferably C_{4-10} α -olefin monomers or ethylene. The process of the invention is particularly useful for the polymerization of ethylene and hex-1-ene.

Preferably the polymer product has ethylene as the major monomer, i.e. at least 50% by number monomer residues being of ethylene, more preferably at least 50% by weight being ethylene residues.

It is also within the scope of the invention to employ a catalyst system which is capable of producing comonomer without comonomer addition. The catalyst systems herein described may thus be used for olefin polymerization, e.g. ethylene polymerization, with the addition of a comonomer and/or *in situ* comonomer production. The term "polymerization" is thus

used herein to include both homo- and co-polymerization.

The catalyst material used in the method of the invention is characterised by having different types, preferably two different types, of active polymerization sites having a significantly different ratio between propagation and termination rates for olefin polymerization and different degrees of incorporation of comonomer. The catalyst material thus conveniently comprises at least two different single-site catalysts. Most preferably the catalyst material consists essentially of two different types of catalyst, preferably two different single-site catalysts.

Typically, the catalyst materials for use in the invention are organometallic or other coordination compounds capable of olefin polymerization, e.g. metallocene catalysts, chromocene-silica catalysts, etc. The different catalysts may be of the same or different types, e.g. metallocene plus metallocene, organometallic non-metallocene plus metallocene, etc. Most preferably, the catalyst materials will be selected from a single catalyst family, i.e. these will be of the same type. In general, at least one catalyst site, preferably both catalyst sites, will comprise at least one π -bonded ligand.

Preferably the catalyst comprises two or more, most preferably two, cyclopentadienyl-containing organometallic compounds, e.g. metallocenes. Especially preferably, the catalyst comprises at least one, preferably two metallocenes comprising a group 4, 5 or 6 metal, especially a group 4 metal. In cases where polymer components having different weight average molecular weights are desired, the catalyst material capable of producing the lower molecular weight fraction will preferably comprise a group 4 metal. Typically this will comprise a group 4 metallocene.

At least one, and preferably at least two of the catalysts, will typically comprise single site catalysts

such as the catalytically effective metal: η -ligand complexes, i.e. complexes in which the metal is complexed by the extended Π -orbital system of an organic ligand. Metallocenes are an example of complexes in which a metal is complexed by two η -ligands. In the present invention metal: η -ligand complexes may be used where the metal is complexed by one, two or more η -ligands. The use of twin η -ligand metallocenes and single η -ligand "half metallocenes" (e.g. those developed by Dow) is particularly preferred. However, the term metallocene as used herein is used to refer to all such catalytically active complexes containing one or more η -ligands. The metal in such complexes is preferably a group 4, 5, 6, 7 or 8 metal or a lanthanide or actinide, especially a group 4, 5 or 6 metal, particularly Zr, Hf, Ti or Cr. The η -ligand preferably comprises a cyclopentadienyl ring, optionally with a ring carbon replaced by a heteroatom (e.g. N, B, S or P), optionally substituted by pendant or fused ring substituents and optionally linked by a bridge (e.g. a 1 to 4 atom bridge such as $(\text{CH}_2)_2$, $\text{C}(\text{CH}_3)_2$ or $\text{Si}(\text{CH}_3)_2$) to a further optionally substituted homo or heterocyclic cyclopentadienyl ring. The ring substituents may for example be halo atoms or alkyl groups optionally with carbons replaced by heteroatoms such as O, N and Si, especially Si and O and optionally substituted by mono or polycyclic groups such as phenyl or naphthyl groups. Examples of such homo or heterocyclic cyclopentadienyl ligands are well known from the scientific and patent literature, e.g. from the published patent applications of Hoechst, Montell, Borealis, Exxon, and Dow, for example EP-A-416815, WO 96/04290, EP-A-485821, EP-A-485823, US-A-5276208 and US-A-5145819.

Thus the η -bonding ligand may for example be of formula I



where Cp is an unsubstituted, mono-substituted or polysubstituted homo or heterocyclic cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, benzindenyl, cyclopenta[1]phenanthrenyl, azulenyl, or octahydrofluorenyl ligand; m is zero or an integer having a value of 1, 2, 3, 4 or 5; and where present each Y which may be the same or different is a substituent attached to the cyclopentadienyl ring moiety of Cp and selected from halogen atoms, and alkyl, alkenyl, aryl, aralkyl, alkoxy, alkylthio, alkylamino, (alkyl)₂P, alkylsilyloxy, alkylgermyloxy, acyl, acyloxy and amido groups or one Y comprises an atom or group providing an atom chain comprising 1 to 4 atoms selected from C, O, S, N, Si and P, especially C and Si (e.g. an ethylene group) to a second unsubstituted, mono-substituted or polysubstituted homo or heterocyclic cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl ligand group.

In the η -bonding ligands of formula I, the rings fused to the homo or hetero cyclopentadienyl rings may themselves be optionally substituted e.g. by halogen atoms or groups containing 1 to 10 carbon atoms.

Many examples of such η -bonding ligands and their synthesis are known from the literature, see for example: Möhring et al. *J. Organomet. Chem* **479**:1-29 (1994), Brintzinger et al. *Angew. Chem. Int. Ed. Engl.* **34**:1143-1170 (1995).

Examples of suitable η -bonding ligands include the following:

cyclopentadienyl, indenyl, fluorenyl, pentamethyl-cyclopentadienyl, methyl-cyclopentadienyl, 1,3-dimethyl-cyclopentadienyl, i-propyl-cyclopentadienyl, 1,3-di-i-propyl-cyclopentadienyl, n-butyl-cyclopentadienyl, 1,3-di-n-butyl-cyclopentadienyl, t-butyl-cyclopentadienyl, 1,3-di-t-butyl-cyclopentadienyl, trimethylsilyl-cyclopentadienyl, 1,3-di-trimethylsilyl-cyclopentadienyl, benzyl-cyclopentadienyl, 1,3-di-

benzyl-cyclopentadienyl, phenyl-cyclopentadienyl, 1,3-di-phenyl-cyclopentadienyl, naphthyl-cyclopentadienyl, 1,3-di-naphthyl-cyclopentadienyl, 1-methyl-indenyl, 1,3,4-tri-methyl-cyclopentadienyl, 1-i-propyl-indenyl, 1,3,4-tri-i-propyl-cyclopentadienyl, 1-n-butyl-indenyl, 1,3,4-tri-n-butyl-cyclopentadienyl, 1-t-butyl-indenyl, 1,3,4-tri-t-butyl-cyclopentadienyl, 1-trimethylsilyl-indenyl, 1,3,4-tri-trimethylsilyl-cyclopentadienyl, 1-benzyl-indenyl, 1,3,4-tri-benzyl-cyclopentadienyl, 1-phenyl-indenyl, 1,3,4-tri-phenyl-cyclopentadienyl, 1-naphthyl-indenyl, 1,3,4-tri-naphthyl-cyclopentadienyl, 1,4-di-methyl-indenyl, 1,4-di-i-propyl-indenyl, 1,4-di-n-butyl-indenyl, 1,4-di-t-butyl-indenyl, 1,4-di-trimethylsilyl-indenyl, 1,4-di-benzyl-indenyl, 1,4-di-phenyl-indenyl, 1,4-di-naphthyl-indenyl, methyl-fluorenyl, i-propyl-fluorenyl, n-butyl-fluorenyl, t-butyl-fluorenyl, trimethylsilyl-fluorenyl, benzyl-fluorenyl, phenyl-fluorenyl, naphthyl-fluorenyl, 5,8-dimethyl-fluorenyl, 5,8-di-i-propyl-fluorenyl, 5,8-di-n-butyl-fluorenyl, 5,8-di-t-butyl-fluorenyl, 5,8-di-trimethylsilyl-fluorenyl, 5,8-di-benzyl-fluorenyl, 5,8-di-phenyl-fluorenyl and 5,8-di-naphthyl-fluorenyl.

Besides the η -ligand, the catalyst complex used according to the invention may include other ligands; typically these may be halide, hydride, alkyl, aryl, alkoxy, aryloxy, amide, carbamide or other two electron donor groups.

In a preferred embodiment the catalyst composition comprises two η -ligand catalysts, preferably a combination of unbridged and bridged bis- η -liganded complexes of group 4, 5 or 6 metals, e.g. where the unbridged η -ligand complex is a metallocene with two homo or heterocyclopentadienyl ligands which are optionally ring substituted by fused or pendant substituent groups and the bridged η -ligand complex comprises two η -liganding groups joined by a 1 to 4 atom chain. One example of a metallocene combination would

thus be (i) an unbridged biscyclopentadienyl Ti, Zr or Hf compound and (ii) a bridged bis-indenyl Ti, Zr or Hf compound, e.g. substituted Cp_2ZrCl_2 in combination with optionally substituted $\text{CH}_2\text{CH}_2(\text{Ind})_2\text{ZrCl}_2$ or $\text{Si}(\text{CH}_3)_2(\text{Ind})_2\text{ZrCl}_2$. An alternative combination would be a dimethylsilylbis(fluorenyl) Ti, Zr or Hf complex (e.g. optionally substituted $\text{SiMe}_2(\text{fluorenyl})\text{ZrCl}_2$) and a substituted biscyclopentadienyl Ti, Zr or Hf complex. Particularly preferred catalyst combinations for use in the invention include (i) $\text{Cp}^*_2\text{ZrCl}_2$ (Cp^* = pentamethyl substituted cyclopentadienyl) and rac-dimethyl silylbis(2-methyl-4-phenyl)indenyl zirconium dichloride; (ii) $\text{Cp}^*_2\text{ZrCl}_2$ and bis(n-butylcyclopentadienyl) hafnium dichloride; and (iii) $(\text{nBuCp})_2\text{ZrCl}_2$ and $\text{Et}(1\text{-Ind})_2\text{HfCl}_2$.

The different types of catalyst sites in the catalyst material used in the process of the invention may be present in substantially equal numbers (i.e. a mole ratio of 1:1, or 1:1:1, etc. for two or three catalyst-type systems). However one catalyst type may be predominant with other catalyst types being present at a relative mol. % of for example 1 to 100% (100% representing a 1:1 mole ratio), preferably 5 to 80%, especially 10 to 70%.

For use in olefin polymerisation, the catalyst material may include one or more co-catalysts or catalyst activators and in this regard any appropriate co-catalyst or activator may be used. It is preferred that the catalyst material is particulate and includes a support or carrier.

Viewed from a further aspect the invention thus provides an olefin polymerisation catalyst system comprising a catalyst in accordance with the invention, together with a co-catalyst.

In a yet further aspect the invention provides a process for producing a polyolefin in which an α -olefin monomer, preferably a C_{2-20} α -olefin, e.g. ethylene, is contacted with a comonomer, preferably a mono or

polyunsaturated C_{2-20} compound, e.g. a C_{2-10} α -olefin, in the presence of a catalyst or catalyst system according to the invention. Preferably, the invention provides a process for producing a polyolefin in which an α -olefin monomer is contacted with a comonomer in a single polymerization reactor in the presence of a catalyst or catalyst system according to the invention. Most preferably, the process is performed in the presence of two or more, e.g. two, simultaneously present types of catalyst. Polyolefin products obtained by such processes form a further aspect of the invention.

Examples of co-catalysts and catalyst activators suitable for use in the invention include aluminium trialkyls (e.g. triethylaluminium), aluminoxanes such as methylaluminoxane, cationic activators such as boron containing compounds, transition metal compounds (e.g. halogenide compounds), magnesium compounds, group III organometallic compounds, e.g. aluminium or boron based compounds. Such materials may be solids, liquids or may be in solution in a liquid phase of the catalyst material which may be a solution, a solid, a dispersion, a suspension, a slurry, etc.

Preferred aluminoxanes include C_{1-10} alkyl aluminoxanes, in particular methyl aluminoxane (MAO) and aluminoxanes in which the alkyl groups comprise isobutyl groups optionally together with methyl groups. Such aluminoxanes may be used as the sole co-catalyst or alternatively may be used together with other co-catalysts. Thus besides or in addition to aluminoxanes other cation complex forming catalyst activators may be used. In this regard mention may be made of the silver and boron compounds known in the art. What is required of such activators is that they should react with the η -liganded complex to yield an organometallic cation and a non-coordinating anion (see for example the discussion on non-coordinating anions J^- in EP-A-617052 (Asahi)).

Aluminoxane co-catalysts are described by Hoechst

in WO 94/28034. These are cyclic oligomers of cage-like structure having up to 40, preferably 3 to 20, $\{Al(R'')O\}$ repeat units (where R'' is hydrogen, C₁₋₁₀ alkyl (preferably methyl and/or isobutyl) or C₆₋₁₈ aryl or mixtures thereof).

The catalyst material may if desired include a support, e.g. an inorganic or organic carrier material, preferably a solid particulate material and also preferably a porous material. Conventional catalyst support materials may be used in this regard, e.g. porous inorganic or organic materials, for example oxides such as silica, alumina, silica-alumina, silica with Ti, zirconia, etc, non-oxides such as magnesium halides, e.g. MgCl₂, aluminium phosphate, zeolites etc, and polymers such as polystyrene, polymethacrylate, polystyrene-divinylbenzene and polyolefins such as polyethylene and polypropylene.

Where an inorganic support material is used, this will preferably be treated, e.g. thermally or chemically to remove surface hydroxyl.

Where a support material is used, this will especially preferably be used to carry more than one type of catalytic site, i.e. so that a particulate support will present two or more different active polymerization sites on the same particles.

Where different types of catalytic sites are present on the same carrier particles, it is preferred that the ratio between the different types of site be substantially uniform within the particles, i.e. it is preferred that the ratio be the same on the surface as it is at different depths within the particles and that the ratio be substantially uniform between the particles.

The process of the invention may be carried out in a single reactor or in a series of two or more reactors. Due to the complexities of operation of multi-reactor systems, the polymerization process of the invention is

most advantageously effected continuously in a single reactor section, particularly preferably as a single stage or one-step polymerization. Multi-stage polymerization reactions may, however, be used in cases where it is desired to produce more complex polymer products.

During a single step polymerization all conditions in the reaction vessel remain essentially constant. These include, for example, temperature, pressure, concentration of comonomer and hydrogen, etc. In a single step procedure, the catalysts and optional cocatalyst may be fed into the reactor concurrently, separately or in the form of a blend.

The or each polymerization stage may be effected using conventional procedures, e.g. as a slurry, gas phase, solution or high pressure polymerization. Slurry polymerisation includes polymerisation at slightly supercritical conditions. Mixed gas phase and slurry reactors are preferred. Slurry polymerization (e.g. bulk polymerization) is preferably effected, e.g. in a tank reactor or more preferably a loop reactor. The polymerization process may use a series of two or more reactors, preferably loop and/or gas phase reactors, e.g. a combination of loop and loop, gas phase and gas phase or most preferably loop and gas phase reactors. In slurry reactors, if a major monomer is propylene this may also function as a solvent/diluent as well as a reagent. If the major monomer is ethylene, a non-polymerizable organic compound, e.g. a C₃₋₁₀ alkane, for example propane or isobutane, may be used as a diluent. Where this is done, the volatile non-reacted or non-reactive materials will desirably be recovered and reused.

The polymerization process of the invention may be a multi-stage process. Where the process of the invention is effected in a single reactor vessel, the various polymerization stages will conveniently be

effected using different monomer/comonomer mixtures and optionally different process conditions (i.e. temperature, pressure, reaction time, etc.). In each reaction stage, the different types of active polymerization sites on the catalyst material will generate polymers of different molecular weight distribution having different levels of comonomer incorporation.

Whether effected as a multi-stage or single stage process, the resulting polymer will be an intimately mixed polymer mixture, e.g. having a multi-modal or broad molecular weight distribution or otherwise containing two intermingled populations of polymers with different comonomer distributions.

The reactor used in the process of the invention may conveniently be any of the conventionally used polymerization reactors, e.g. reactors for solution polymerization, slurry tank or slurry loop polymerization or gas phase polymerization, etc.

For slurry reactors, the reaction temperature will generally be in the range 60 to 110°C (e.g. 85-110°C), the reactor pressure will generally be in the range 5 to 80 bar (e.g. 25-65 bar), and the residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C. In such reactors, polymerization may if desired be effected under supercritical conditions, especially in loop reactors.

For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C (e.g. 70 to 110°C), the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen together with monomer (e.g. ethylene or propylene).

For solution phase reactors, the reaction

temperature used will generally be in the range 130 to 270°C, the reactor pressure will generally be in the range 20 to 400 bar and the residence time will generally be in the range 0.1 to 1 hour. The solvent used will commonly be a hydrocarbon with a boiling point in the range 80-200°C.

The catalyst material may be introduced into the reactor used in the process of the invention as a single material containing all the components of the catalyst material or as two or more materials which together contain all of the components of the catalyst material or which together interact to generate the catalyst material. It is preferred to introduce the catalyst material as a single material which may be a solution, a solid, a dispersion, a suspension or a slurry, etc.

Generally the quantity of catalyst used will depend upon the nature of the catalyst, the reactor types and conditions and the properties desired for the polymer product. Conventional catalyst quantities, such as described in the publications referred to herein, may be used.

In the process of the invention, hydrogen may be used to further control the molecular weight of the olefin copolymer produced in the reactor. Molecular weight control may be effected through control of the hydrogen concentration or, alternatively, through control of the hydrogen consumption during the polymerization process. In such cases, it is preferable to use a catalyst system which is responsive to hydrogen. Control over the molecular weight of the polymer can be readily achieved by monitoring the hydrogen and monomer consumption, i.e. for hydrogen the difference between hydrogen input and hydrogen output and for monomer the difference between monomer input and output. The ratio of hydrogen consumption to monomer consumption can be correlated well with polymer molecular weight and the product molecular weight can

accordingly be adjusted to the desired level using this correlation and by appropriate adjustment of the hydrogen and monomer feed rate levels.

The process of the invention may optionally comprise further stages in addition to that of polymerization, e.g. drying steps; blending of the polymer product with one or more further materials, e.g. further polymers, antioxidants, radiation (e.g. UV-light) stabilizers, antistatic agents, fillers, plasticizers, carbon black, colors, etc.; granulation, extrusion and pelletization; etc.

The final polymer product of the process of the invention will preferably have a MFR of 0.1 to 500, a weight average molecular weight (Mw) of 30,000 to 500,000 and a melting point of 100-165°C (e.g. 70-136°C for copolymers of ethylene and 120 to 165°C for copolymers of propylene).

This polymer can be formulated together with conventional additives, e.g. antioxidants, UV-stabilizers, colors, fillers, plasticizers, etc. and can be used for fibre or film extrusion or for raffia, or for pipes, or for cable or wire applications or for moulding, e.g. injection moulding, blow moulding, rotational moulding, etc., using conventional moulding and extrusion equipment.

The process of the invention gives rise to polymer products with improved molecular weight and comonomer distributions. The process of the invention may be used with particular advantage to tailor the distribution of molecular weights in the higher molecular weight fraction of the overall polymer and this may be done in such a way as to include comonomer (which may provide side chains and as a result increased strength) primarily in the high molecular weight fraction. For example, using the process of the invention, comonomer may incorporate more into the longer rather than the shorter polymer chains as compared for example with the

product obtained using a Ziegler or Phillips type catalyst in a similar process, so improving the mechanical properties of the polymer product. The presence of a bi-modal or multi-modal distribution at the higher end of the molecular weights, which may be achieved using a multi-stage process, improves the ease of homogenization as the lower molecular weight component of the high molecular weight fraction reduces viscosity of the high molecular weight fraction. Without this low end to it the high molecular weight fraction may give rise to melt homogenization problems, thereby resulting in an inhomogeneous melt.

Thus the process of the invention allows the user to tailor the placement of comonomer into the high molecular weight fraction of the polymer and also to tailor the molecular weight profile of the high molecular weight fraction of the polymer.

The polymers produced using the catalysts or processes according to the invention have a number of beneficial properties relative to polymers produced using conventional techniques. For example, where a comonomer such as but-1-ene or hex-1-ene is used, this incorporates primarily into the longer rather than the shorter polymer chains so improving the mechanical and processing properties of the polymer product. Thus the ratio in the short chain branching frequency (the number of branches per 1000 carbons) between the high and low molecular weight fractions of the polymer may typically be at least 3, preferably at least 5, most preferably at least 10.

Furthermore, the polymer product has a high degree of particle to particle homogeneity. The homogeneity of the polymer is often a matter of particular concern to end users since inhomogeneity may give rise to phenomena known as fish eyes, gels or white spots. This is particularly important for films but is also important for wires, cables, blow moulded products, injection

moulded products, rotational moulded products, pipes and fibres.

The production of highly homogeneous multi-modal, e.g. bi-modal, olefin polymers having controlled comonomer incorporation in a single polymerization stage has up to now been problematical. The use of simultaneous coimpregnation of catalyst support particles in the process of the invention to produce supported catalysts having two or more catalytic sites with different comonomer propensities results in supported catalysts which can be used to produce highly homogeneous polymers in a multi-stage, preferably in a single stage, polymerization.

Thus viewed from a further aspect the invention provides a polyolefin, preferably an ethene copolymer, especially preferably a polyolefin made in one reactor, comprising at least two polymer components A and B produced by polymerization catalysed by polymerization catalysts having at least two different types of catalytic site, preferably a supported catalyst comprising both such catalysts, where the ratio of comonomer content of component B to that of component A is at least 3, preferably at least 5, more preferably at least 10. Polymer components A and B may have the same or substantially the same weight average molecular weight (Mw), but different comonomer contents. However, preferably comonomer content will increase with molecular weight, i.e. component B will have a higher weight average molecular weight than component A. Preferably, the polymers will be generally free from components having both a higher weight average molecular weight and a lower average comonomer content than another component. Articles produced using such products form a further aspect of the invention.

In a preferred aspect of the invention, component B may be characterised by a comonomer content in the short chains which is substantially the same or relatively

lower than that in the long chains. Alternatively, or in addition, component A may have a similar distribution of comonomer.

Although the invention has been described with particular reference to comonomer incorporation, the processes herein described may find broader applicability. In particular, suitable choice of catalyst materials and process conditions may be used to control incorporation not only of comonomer, but of other polymer chain defects. As used herein, the term "polymer chain defect" is intended to encompass any irregularity in the otherwise regular structure of a given polymer component, e.g. a crystallinity disrupting monomer unit. An example of a polymer chain defect is a monomer unit incorporated in a non-regular configuration, e.g. as in isotactic polypropylene molecules. Appropriate choice of a catalyst material having stereo and non-stereospecific sites may, for example, be used to prepare a polymer having polymer components of different crystallinity. As used herein, the terms "level of polymer chain defect", "polymer chain defect content" and "level of incorporation of polymer chain defect" are used interchangeably and are intended to define the average polymer chain defect content of any given polymer component over its entire molecular weight range, i.e. the average number of polymer chain defects per thousand carbon atoms.

Thus, viewed from a broader aspect the invention provides a process for the preparation of an olefin polymer, wherein olefin polymerization is effected, preferably in a single reactor section, in the presence of an olefin polymerization catalyst having catalytic sites with different propensities for incorporation of polymer chain defects, preferably wherein olefin polymerization is effected in the presence of an olefin polymerization catalyst capable of producing polymers in which the polymer chain defect content of a first

polymer component is at least 3, preferably at least 5, e.g. at least 10, times higher than that of a second polymer component.

In a still further aspect the invention provides a multi-site polymerization catalyst, preferably a dual-site catalyst, having catalytic sites capable of producing under essentially constant polymerization conditions a polymer comprising at least first and second polymer components having different levels of polymer chain defects, preferably different levels of crystallinity-disrupting monomer units, preferably wherein said levels of polymer chain defects differ by a factor of at least 3, preferably at least 5, e.g. at least 10.

In a yet still further aspect the invention provides a polyolefin, preferably an ethene copolymer, especially preferably a polyolefin made in one reactor, comprising at least two polymer components A and B produced by polymerization catalysed by polymerization catalysts having at least two different catalytic sites, where the ratio of polymer chain defect content of component B to that of component A is at least 3, preferably at least 5, more preferably at least 10.

The polymers produced in accordance with the process of the invention may be analysed by techniques well known in the art. Techniques suitable for isolating individual fractions of a sample of the copolymer include Temperature Rising Elution Fraction (TREF). DSC, preferably SIST (Stepwise Isothermal Segregation Technique) may be used to measure co-monomer content (see J.A. Parker, D.C. Bassett, R.H. Olley & P. Jääskeläinen, Polymer 35 (1994) 4140). There are several methods known in the art for determining MWD of a particular polymer sample. Typically, the molecular weight distribution can be determined by Gel Permeation Chromatography (GPC).

All of the documents referred to herein are hereby

incorporated by reference.

The invention will now be described further with reference to the following non-limiting Examples and the attached Figures in which:

Figure 1 shows DSC curves for polymers produced using conventional single site catalyst systems;

Figures 2-5 and 7 show DSC curves for polymers in accordance with the invention produced using dual site catalyst systems and corresponding DSC curves for polymers produced using conventional single site catalyst systems;

Figure 6 shows a GPC curve for a polymer produced in accordance with the invention and corresponding GPC curves for polymers produced using conventional single site catalyst systems.

In the following Examples, the following abbreviations are used:

Cp* = pentamethyl-substituted cyclopentadienyl ligand, $(\text{CH}_3)_5\text{Cp}$.

Example 1 - Preparation of Catalysts

Supported Catalyst (A)

A catalyst solution was prepared by mixing the following chemicals:

- 0.0024 g rac-dimethyl silylbis(2-methyl-4-phenyl)indenyl zirconium dichloride
- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ, a porous particulate silica supplied by Grace company. The silica had been previously calcined in a flow of dry air at 600°C. The catalyst solution was added dropwise in a ratio of 2 g carrier to 3.2 ml catalyst solution. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 60 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

Supported Catalyst (B)

A catalyst solution was prepared by mixing the following chemicals:

- 0.0248 g Cp*₂ZrCl₂
- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ as described above. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 90 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

Supported Catalyst (C)

A catalyst solution was prepared by mixing the following chemicals:

- 0.0248 g Cp*₂ZrCl₂
- 0.0028 g rac-dimethyl silylbis(2-methyl-4-phenyl)indenyl zirconium dichloride
- 2.2 ml MAO solution (30 wt% MAO in toluene)

- 1 ml toluene.

The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ as described above. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 90 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

Supported Catalyst (D)

A catalyst solution was prepared by mixing the following chemicals:

- 0.002 g bis(n-butylcyclopentadienyl) hafnium dichloride
- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ as described above. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 120 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

Supported Catalyst (E)

A catalyst solution was prepared by mixing the following chemicals:

- 0.0244 g Cp^*ZrCl_2
- 0.002 g bis(n-butylcyclopentadienyl) hafnium

dichloride

- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ as described above. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 120 minutes, the mixture was dried by nitrogen flow, to yield a supported catalyst.

Example 2 - Polymerization

Ethylene polymerization using catalysts (A) to (E) was carried out in a 2 L reactor. Isobutane (1 litre) containing 0.02 wt% hexene and the catalyst was charged into the reactor and the temperature and pressure brought up to the desired levels.

Pure ethylene gas was added through a pressure control valve and polymerization carried out under the following conditions: total pressure = 24 bars, temperature = 80°C and polymerization time = 60 minutes.

The results are set out in Table 1 below.

Table 1

	Catalyst (A)	Catalyst (B)	Catalyst (C)	Catalyst (D)	Catalyst (E)
Catalyst type	single site	single site	dual site	single site	dual site
Catalyst	SiMe ₂ (2-Me, 4-Ph Ind) ₂ ZrCl ₂	(Cp*) ₂ ZrCl ₂	(Cp*) ₂ ZrCl ₂ /SiMe ₂ (2-Me, 4-Ph Ind) ₂ ZrCl ₂	(nBuCp) ₂ HfCl ₂	(Cp*) ₂ ZrCl ₂ / (nBuCp) ₂ HfCl ₂
Loading (%)	Normal	Normal	Normal	Normal	Normal
Carrier, drying temperature (°C)	55SJ/600°C	55SJ/600°C	55SJ/600°C	55SJ/600°C	55SJ/600°C
Catalyst weight (g)	0.424	0.31	0.331	0.478	0.417
Reaction temp. (°C)	80	80	80	80	80
Reaction press. (bar)	24	24	24	24	24
Ethene partial press. (bar)	10	10	10	10	10
C ₆ /Ethene Cascade (wt. % C ₆)	5	5	5	5	5
Ind. time (min*cat weight)	0	0	0	0	0
Total run time (mins)	60	60	60	60	60
Polymer weight (g)	177	41	34	235	70
Productivity (g polymer/g catalyst)	417	132	103	492	168
Activity (g/g h)	1565	132	103	492	168
GPC, Mw	710000	345000	255000	570000	405000
GPC, Mn	150000	53000	60000	165000	80000
GPC, MWD	4.7	6.5	4.3	3.5	5.1
Remarks	Fouling			Fouling	

DSC analyses with SIST (Stepwise Isothermal Segregation Technique) annealing were carried out under the following conditions:

Step	Temperature (°C)	Time at temperature (mins)	Rate to next temperature (K/min)
1	200	5	200
2	131	120	200
3	118	120	200
4	105	120	200
5	92	120	200
6	79	120	200
7	66	120	1
8	10		

Each sample was then heated at a rate of 10K/min to produce the melting curves given in attached Figures 1 to 5.

Figure 1 shows melting curves for the polymers produced using catalysts (A) and (D). The same height of curve at different melting temperatures is indicative of a greater proportion of the polymer at the lower melting temperature than at the higher. This is due to the difference in crystallinity and hence lower specific melting enthalpy at lower melting temperatures. The height of the curves in Figure 1 therefore indicates the relative concentration of the polymer at each melting temperature. This means that the product produced using catalyst (A) has lower crystallinity than that produced using catalyst (D), and the cross-over point is about 65°C. Both of these polymers were found to exhibit a degree of fouling in the reactor.

Figures 2 and 3 show melting curves for the polymer produced using the dual site catalyst (E) and for the polymers produced using the corresponding single site catalysts, (B) and (D). The dual site catalyst did not exhibit fouling. This is considered surprising given that the low crystallinity polymer components each have melting temperatures lower than the polymerization temperature. The dual site DSC curves correspond to a product having low crystallinity components and correspond well with the melting curves for those products produced from the individual catalyst components. The shift of the main peak may be explained by co-crystallisation.

Figures 4 and 5 show melting curves for the polymer produced using the dual site catalyst (C) and for the polymers produced using the corresponding single site catalysts, (A) and (B). The dual site catalyst did not exhibit fouling.

In Figures 1 to 5, the numbers appearing above the temperature scale represent the % by weight (calculated) of hexene corresponding to that melting temperature. These numbers have been calculated from a calibration based on single site PEs and fractions collected after fractionation according to chemical structure. The calibration was made by a linear approximation of comonomer content (as determined by C-13 NMR) and melting temperature (as determined by DSC) according to the following equation:

$$Y = -0.5228.t + 68.205$$

where Y is wt.% hexene and t is the melting temperature. Similarly, comonomer content may be determined according to the equation:

$$Y = -0.8714.t + 113.67$$

where Y is comonomer content (branches per 1000 C atoms) and t is the melting temperature.

GPC analyses were carried out under the following conditions:

Equipment: Waters 150CV plus no. 1115
Detector: Refractive Index (RI) and Viscosity detector
Calibration: Narrow MWD PS (1115-9903)
Columns: 3 x HT6E styragel from Waters (140°C)

Results are given in attached Figure 6. The high molecular weight tail for the polymer produced using catalyst (E), marked (*) is to be noted. This is considered to be higher than would be expected from a simple summation of molecular weights and may be evidence of a general synergistic effect of the dual site catalyst systems in accordance with the invention.

The low crystallinity/high comonomer/high Mw tail profile confirms that a product comprising a mixture of low and high molecular weight, homo and copolymers, may be produced in accordance with the invention in a single reaction stage.

Example 3 - Catalyst Preparation

Supported Catalyst (F)

The catalyst was produced analogously to supported catalyst (D) except that Zirconium was used in place of Hafnium and the relative amounts were adjusted to produce a supported catalyst product comprising 0.027 mmol (nBuCp)₂ZrCl₂/g carrier; and 5.6 mmol Al (from

MAO)/g carrier.

Supported Catalyst (G)

A dually impregnated carrier was prepared as above using a catalyst solution prepared by mixing 0.044 g $(n\text{BuCp})_2\text{ZrCl}_2$, 0.0269 g $\text{Et}(1\text{-Ind})_2\text{HfCl}_2$, 1.2 ml MAO solution (30 wt% MAO in toluene from Albemarle SA), and 0.4 ml toluene.

By calculation the supported catalyst product comprised 0.014 mmol $(n\text{BuCp})_2\text{ZrCl}_2/\text{g}$ carrier; 0.0531 mmol $\text{Et}(1\text{-Ind})_2\text{HfCl}_2/\text{g}$ carrier; and 5.5 mmol Al (from MAO)/g carrier.

Example 4 - Polymerization

Ethylene polymerization using catalysts (F) and (G) was carried out in a 2 L semi-batch reactor (continuous feeding of ethylene).

Isobutane (1 litre) containing hexene and the catalyst was charged into the reactor and the temperature and pressure brought up to the desired levels.

The polymerization process conditions and parameters characterising the polymer product are set out in Table 2 below:

Table 2

Catalyst	Catalyst (F) (single site)	Catalyst (G) (dual site)	Catalyst (G) (dual site)
Pressure (bar)	29	29	29
Temperature (°C)	85	85	85
Run time (min)	60	60	60
Hexene (wt% in isobutane)	2.9	2.9	0.18
Hydrogen	-	-	-
Analyses			
Mw (g/mol)	105,000	130,000	175,000
MWD	2.1	2.4	2.7
Tm (peak) (°C)	122.6	125.2	132.2
ΔH_m	148.0	147.5	181.8
Activity	6692	1533	737

DSC curves for the final polymer products are shown in attached Figure 7. These DSC measurements have been obtained with standard annealing, i.e. crystallisation from 200°C to 0°C with a cooling rate of 10K/min, and melting as for the SIST method.

The polymer made with catalyst (F) with a high hexene concentration during polymerization shows a typical single component co-polymer DSC melting behaviour.

The polymers made with catalyst (G) each contain two components of different crystallinity. This is most obvious on the product made with a high hexene concentration where a clear shoulder in the high crystallinity area is seen. The total curve is also shifted towards higher melting temperatures. This may be due to the high comonomer response from the Hf sites which consume most of the added comonomer, thereby causing a lower incorporation of comonomer in the polymer produced by the Zr sites. For the product made with a low hexene concentration, a disturbance on both sides of the peak can be detected, indicating at least two components.

The product made with catalyst (G) with a high hexene concentration during polymerization has a higher Mw and MWD than that made with catalyst (F). This, together with an increase in melting temperature, and maintained melting enthalpy, is explained by the presence of two polymer fractions, one with a lower Mw and comonomer content than the other.

Claims:

1. A process for the preparation of an olefin polymer, wherein olefin polymerization is effected in the presence of an olefin polymerization catalyst having catalytic sites with different propensities for incorporation of polymer chain defects.
2. A process as claimed in claim 1, wherein olefin polymerization is effected in a single reactor section.
3. A process as claimed in claim 1 or claim 2, wherein olefin polymerization is effected in the presence of an olefin polymerization catalyst capable of producing polymers in which the polymer chain defect content of a first polymer component is at least 3 times higher than that of a second polymer component.
4. A process as claimed in claim 3, wherein olefin polymerization is effected in the presence of an olefin polymerization catalyst capable of producing polymers in which the polymer chain defect content of a first polymer component is at least 5, e.g. at least 10, times higher than that of a second polymer component.
5. A process as claimed in claim 1 or claim 2, wherein olefin polymerization is effected in the presence of an olefin polymerization catalyst having catalytic sites with different propensities for comonomer incorporation.
6. A process as claimed in claim 5, wherein olefin polymerization is effected in the presence of an olefin polymerization catalyst capable of producing polymers in which the comonomer content of a first polymer component is at least 3 times higher than that of a second polymer component.

7. A process as claimed in claim 6, wherein olefin polymerization is effected in the presence of an olefin polymerization catalyst capable of producing polymers in which the comonomer content of a first polymer component is at least 5, e.g. at least 10, times higher than that of a second polymer component.

8. A process as claimed in any preceding claim, wherein the olefin polymerization catalyst is one capable of producing a polymer in which the polymer chain defect or comonomer content of a higher molecular weight component of the polymer is at least 3 times the polymer chain defect or comonomer content of a lower molecular weight component.

9. A process as claimed in claim 8, wherein the olefin polymerization catalyst is one capable of producing a polymer in which the polymer chain defect or comonomer content of a higher molecular weight component of the polymer is at least 5, e.g. at least 10, times the polymer chain defect or comonomer content of a lower molecular weight component.

10. A process as claimed in any preceding claim, wherein at least 90 wt% of the polymer is prepared in a single polymerization stage.

11. A process as claimed in any preceding claim, wherein olefin polymerization is effected in the presence of an olefin polymerization multi-site catalyst, e.g. a dual-site catalyst, capable of producing multi-modal (e.g. bi-modal) molecular weight distribution polymers.

12. An olefin polymer, preferably an olefin copolymer, obtainable by the process as claimed in any one of claims 1 to 11.

13. A multi-site polymerization catalyst, preferably a dual-site catalyst, having catalytic sites capable of producing under essentially constant polymerization conditions polymers comprising at least first and second polymer components having different levels of polymer chain defects.
14. A catalyst as claimed in claim 13 having catalytic sites capable of producing polymers comprising at least first and second polymer components having different levels of polymer chain defects which levels differ by a factor of at least 3.
15. A catalyst as claimed in claim 14 having catalytic sites capable of producing polymers comprising at least first and second polymer components having different levels of polymer chain defects which levels differ by a factor of at least 5, e.g. at least 10.
16. A multi-site polymerization catalyst as claimed in claim 13, preferably a dual-site catalyst, having catalytic sites capable of producing under essentially constant polymerization conditions polymers comprising at least first and second polymer components having different levels of comonomer incorporation.
17. A catalyst as claimed in claim 16 having catalytic sites capable of producing polymers comprising at least first and second polymer components having different levels of comonomer incorporation which levels differ by a factor of at least 3.
18. A catalyst as claimed in claim 17 having catalytic sites capable of producing polymers comprising at least first and second polymer components having different levels of comonomer incorporation which levels differ by a factor of at least 5, e.g. at least 10.

19. A catalyst as claimed in any one of claims 13 to 18, wherein the catalytic site capable of producing a higher molecular weight component of the polymer is capable of a higher level of incorporation of polymer chain defect or of comonomer.

20. A catalyst as claimed in any one of claims 13 to 19 having catalytic sites capable of producing multi-modal (e.g. bi-modal) molecular weight distribution polymers.

21. A catalyst as claimed in any one of claims 13 to 20 comprising two group 4 metallocenes.

22. An olefin polymerization catalyst system comprising a catalyst as claimed in any one of claims 13 to 21, including a co-catalyst.

23. A process for producing a polyolefin in which an α -olefin monomer, e.g. ethylene, is contacted with a comonomer, e.g. a C_{2-10} α -olefin, in the presence of a catalyst or catalyst system as claimed in any one of claims 13 to 22.

24. A polyolefin obtainable by a process as claimed in claim 23.

25. A polyolefin, preferably an ethene copolymer, comprising at least two polymer components A and B produced by polymerization catalysed by polymerization catalysts having at least two different catalytic sites, where the ratio of polymer chain defect content of component B to that of component A is at least 3.

26. A polyolefin as claimed in claim 25 made in one reactor.

27. A polyolefin as claimed in claim 25 or claim 26,

wherein the ratio of polymer chain defect content of component B to that of component A is at least 5, e.g. at least 10.

28. A polyolefin as claimed in claim 25 or claim 26, preferably an ethene copolymer, comprising at least two polymer components A and B produced by polymerization catalysed by polymerization catalysts having at least two different catalytic sites, where the ratio of comonomer content of component B to that of component A is at least 3.

29. A polyolefin as claimed in claim 28, wherein the ratio of comonomer content of component B to that of component A is at least 5, e.g. at least 10.

30. A polyolefin as claimed in any one of claims 25 to 29, wherein polymer component B has a higher weight average molecular weight than component A.

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Figure 1

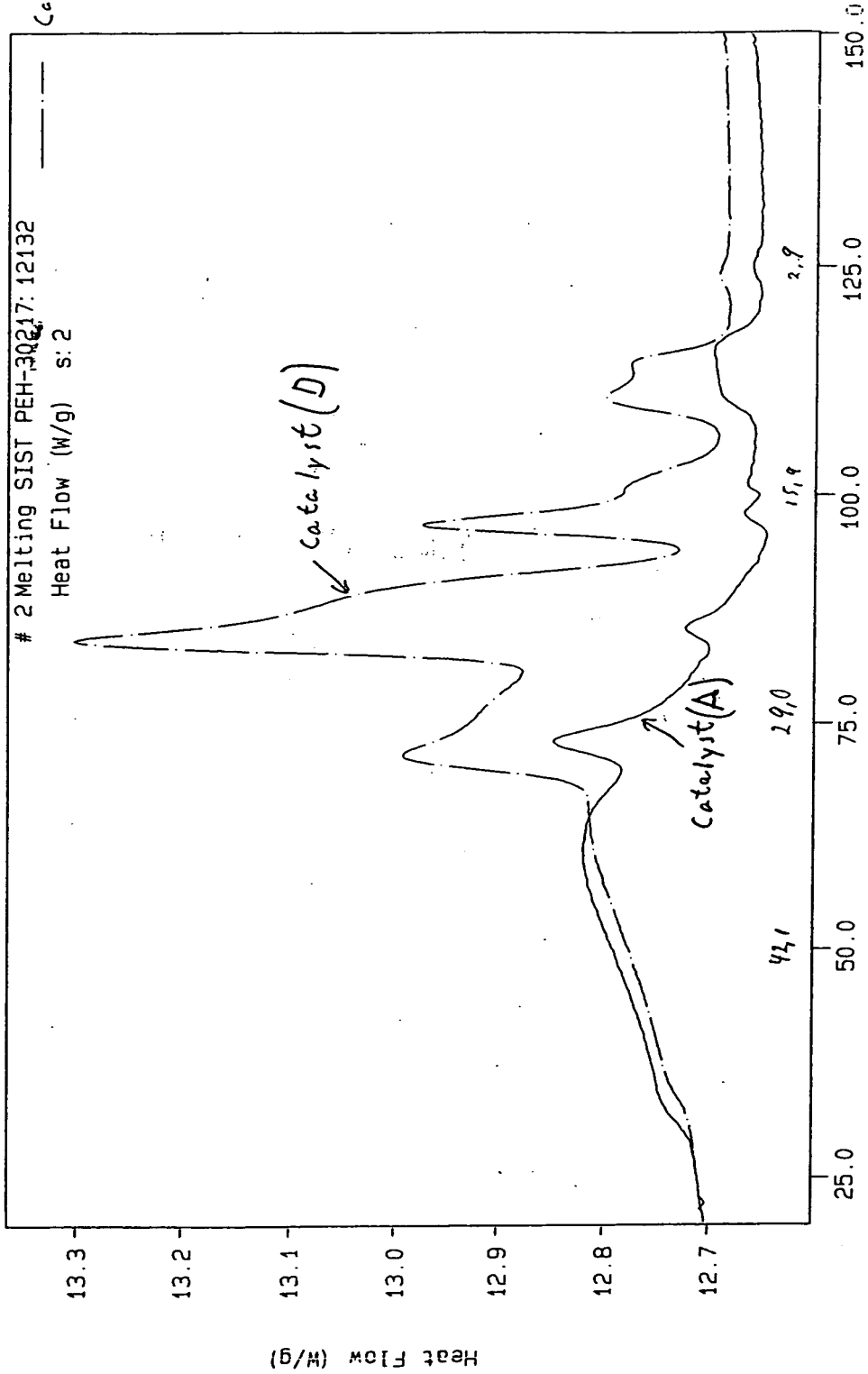
Curve 1: DSC
File info: 12128
Sample Weight: 4.868 mg
Melting SIST PEH-30212

--- Catalyst(A)

1 Melting SIST PEH-30212: 12128
Heat Flow (W/g) s: 2

--- Catalyst(D)

2 Melting SIST PEH-30217: 12132
Heat Flow (W/g) s: 2



tr878C
TEMP: 210.0 C
TEMP: 200.0 C
TIME: 5.0 min RATE: 10.0 C/min
PERKIN-ELMER
7 Series Thermal Analysis System

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Figure 2

Curve 1: DSC

File info: 12124

Sample Weight: 8.896 mg

Melting SIST PEH-30214

1 Melting SIST PEH-30214: 12124

Heat Flow (W/g) s: 2

Catalyst (B)

2 Melting SIST PEH-30217: 12132

Heat Flow (W/g) s: 2

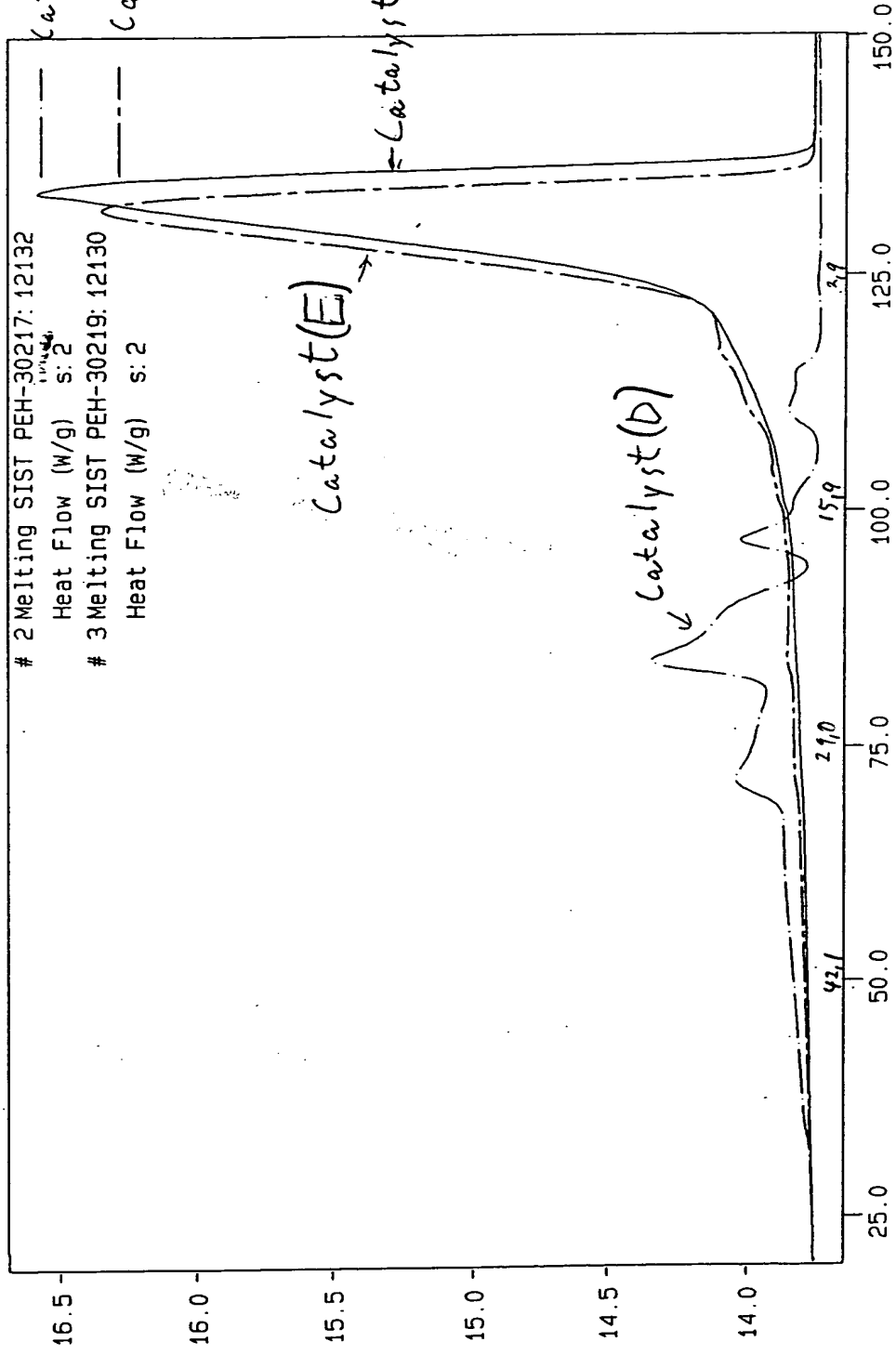
Catalyst (D)

3 Melting SIST PEH-30219: 12130

Heat Flow (W/g) s: 2

Catalyst (E)

Heat Flow (W/g)



Catalyst (E)

Catalyst (D)

Catalyst (B)

tr8789

TEMP1: 200.0 C

TIME1: 5.0 min

RATE1: 10.0 C/min

Temperature (°C)

SS

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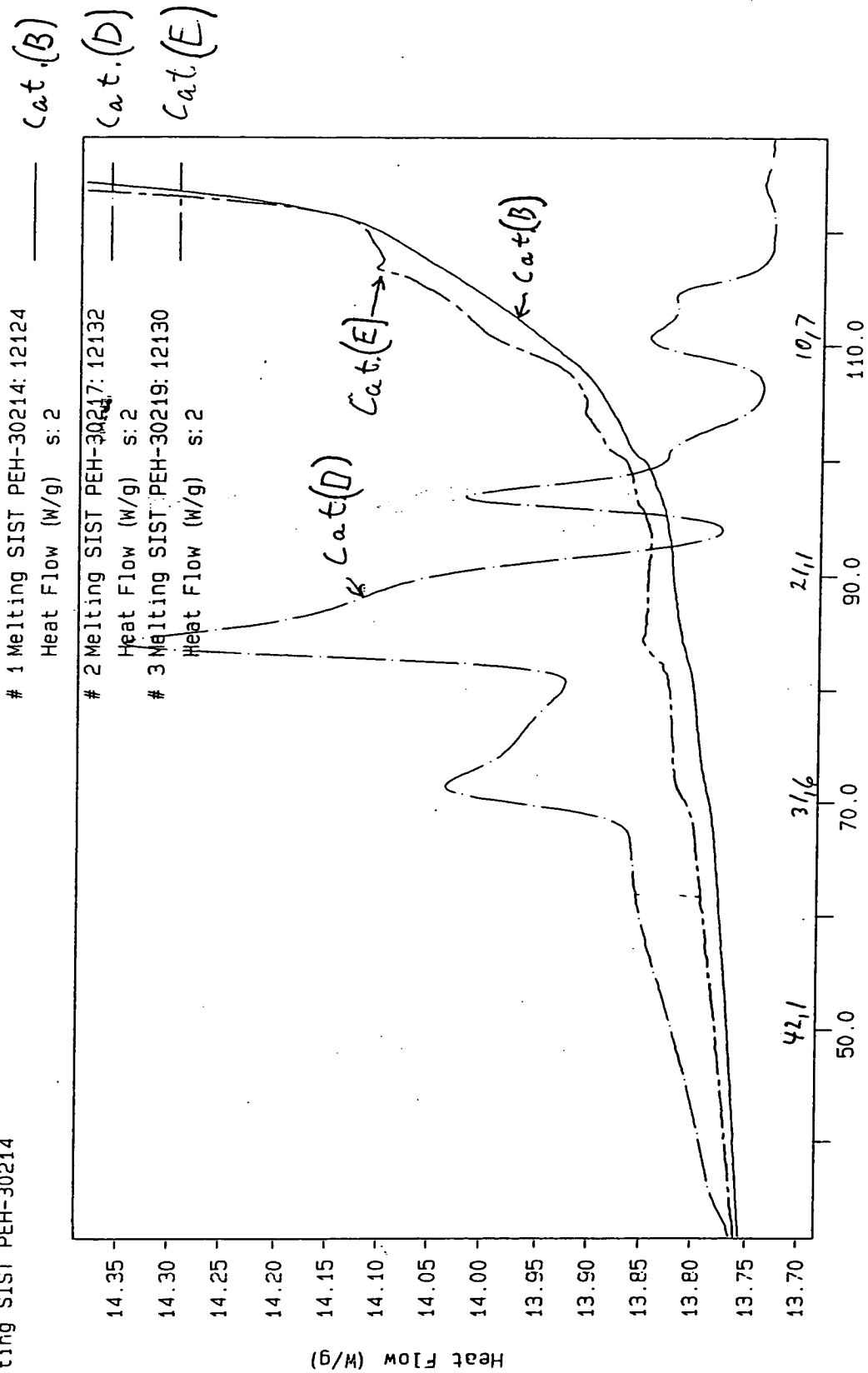
Figure 3

Curve 1: DSC

File info: 12124

Sample Weight: 8.896 mg

Melting SIST PEH-30214



tr878c
 TEMP1: -10.0 C
 TEMP2: 200.0 C
 TIME1: 5.0 min RATE1: 10.0 C/min
 SS PERKIN-ELMER
 7 Series Thermal Analysis System

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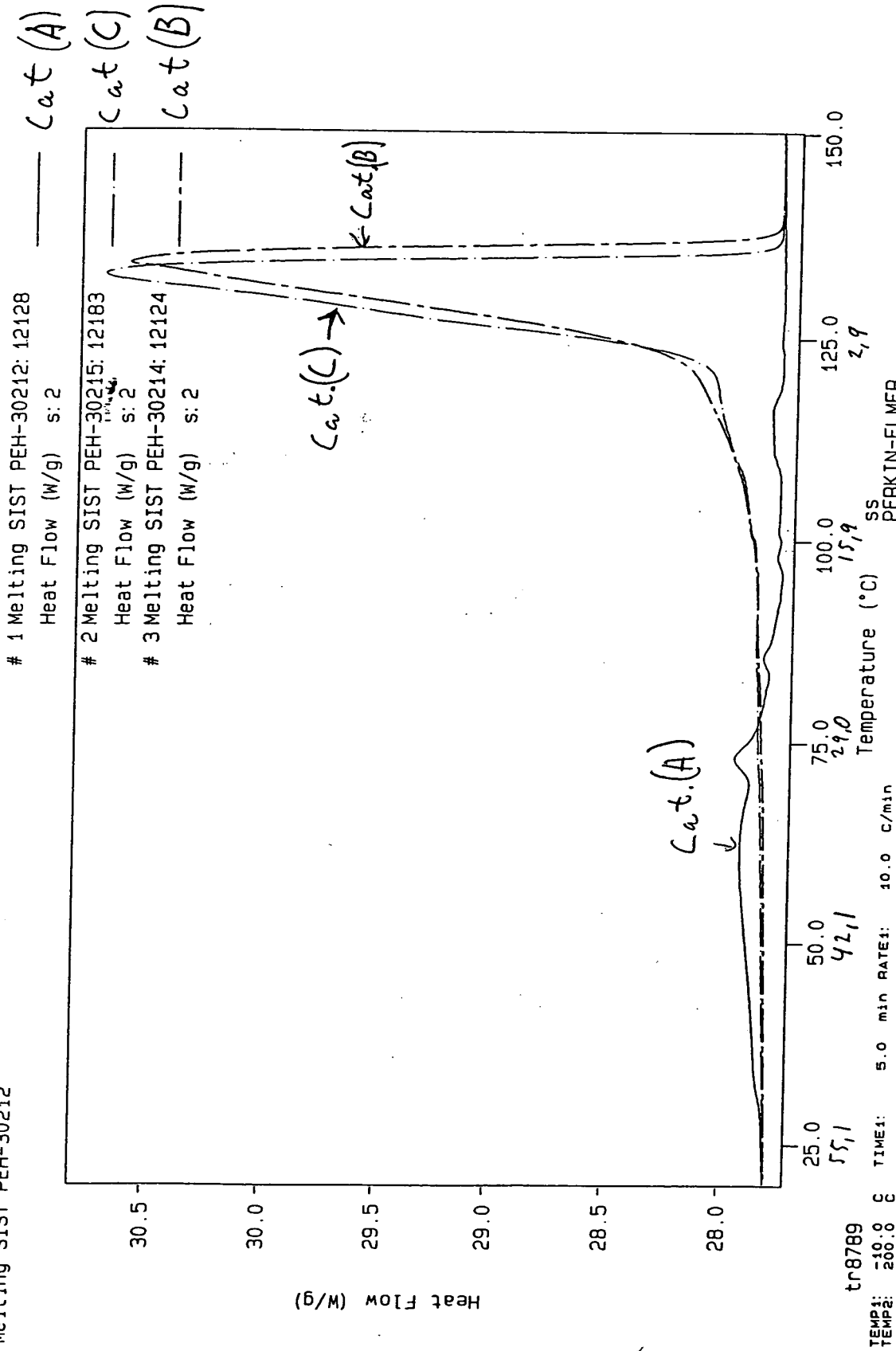
Figure 4

Curve 1: DSC

File info: 12128

Sample Weight: 4.868 mg

Melting SIST PEH-30212



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Figure 5

Curve 1: DSC

File info: 12128

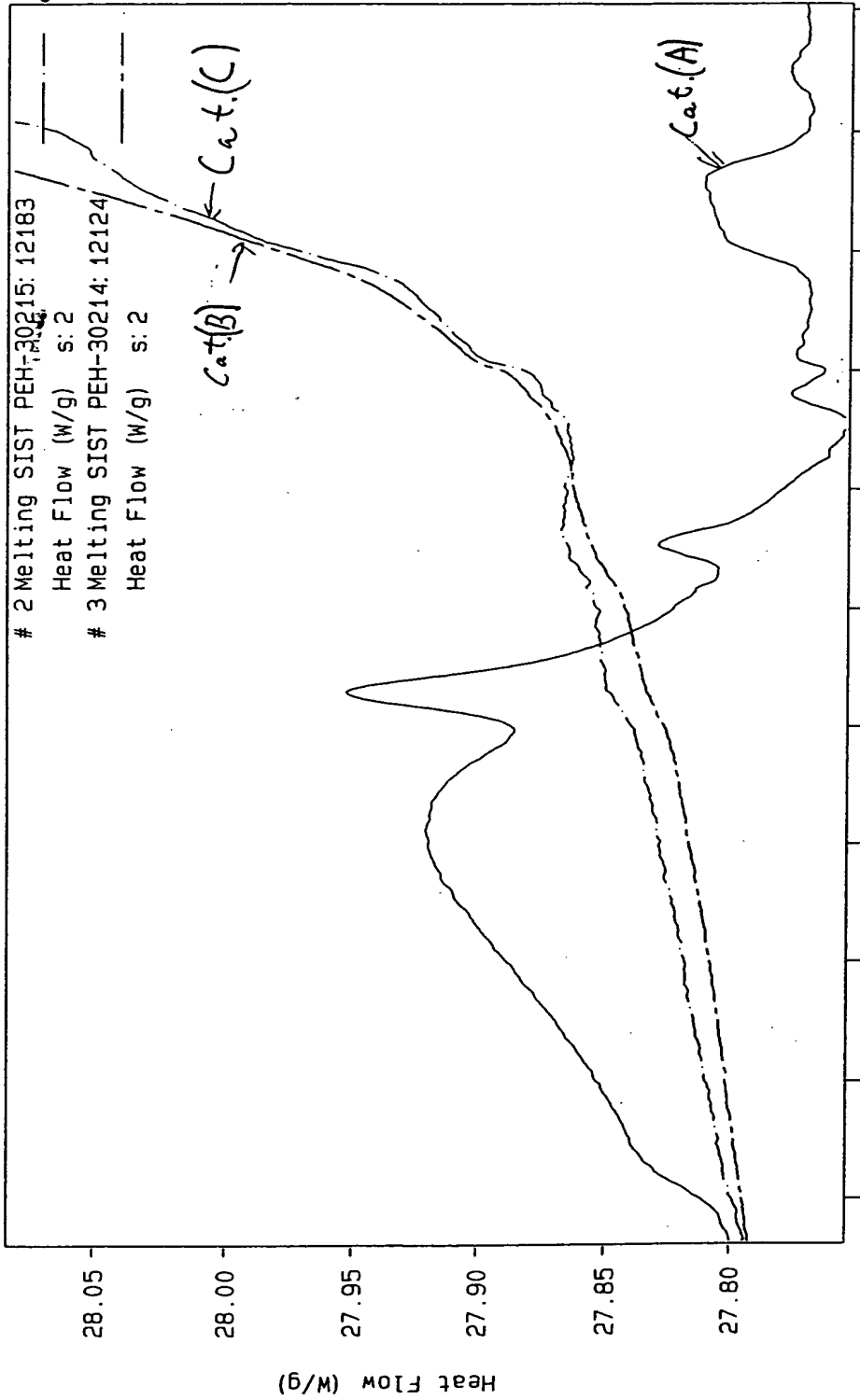
Sample Weight: 4.868 mg

Melting SIST PEH-30212

1 Melting SIST PEH-30212: 12128
Heat Flow (W/g) s: 2 *Cat.(A)*

2 Melting SIST PEH-30215: 12183
Heat Flow (W/g) s: 2 *Cat.(C)*

3 Melting SIST PEH-30214: 12124
Heat Flow (W/g) s: 2 *Cat.(B)*



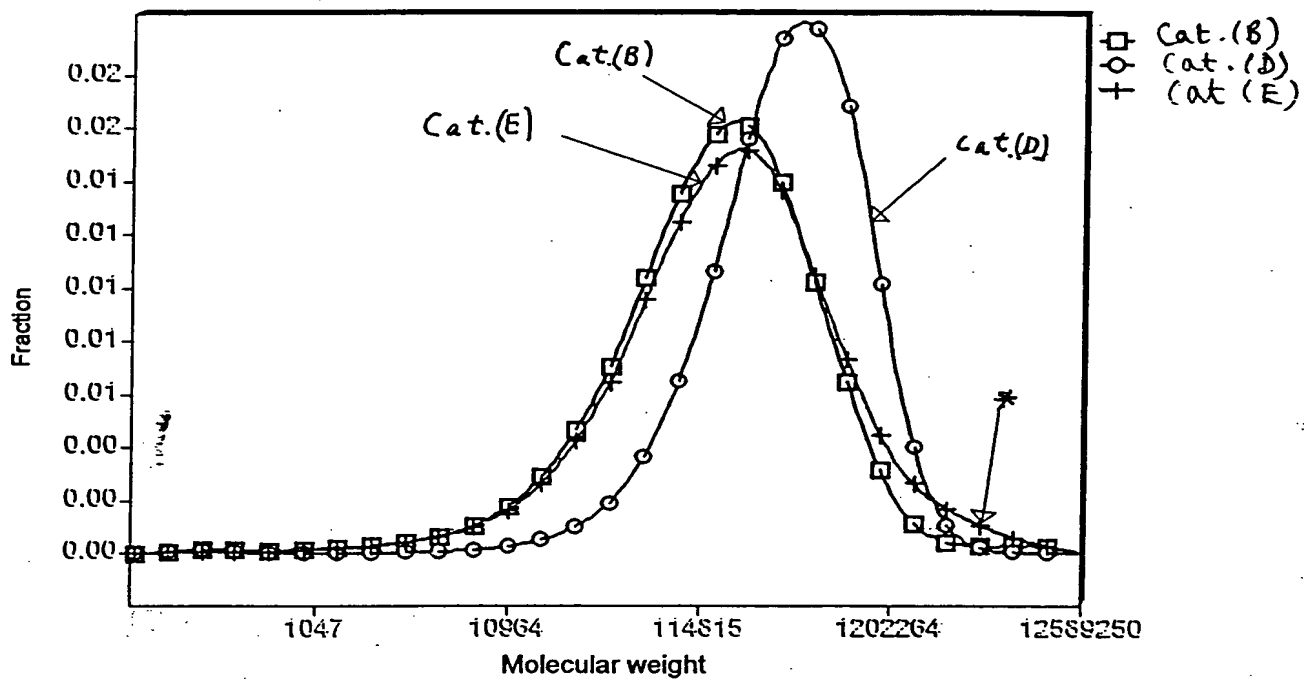
40.0 50.0 60.0 80.0 100.0 120.0
47.3 36.8 26.4 15.9 5.5
Temperature (°C)

tr8789
TEMP1: -40.0 C TIME1: 5.0 min RATE1: 10.0 C/min
TEMP2: 200.0 C

SS PERKIN-ELMER
7 Series Thermal Analysis System

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Figure 6



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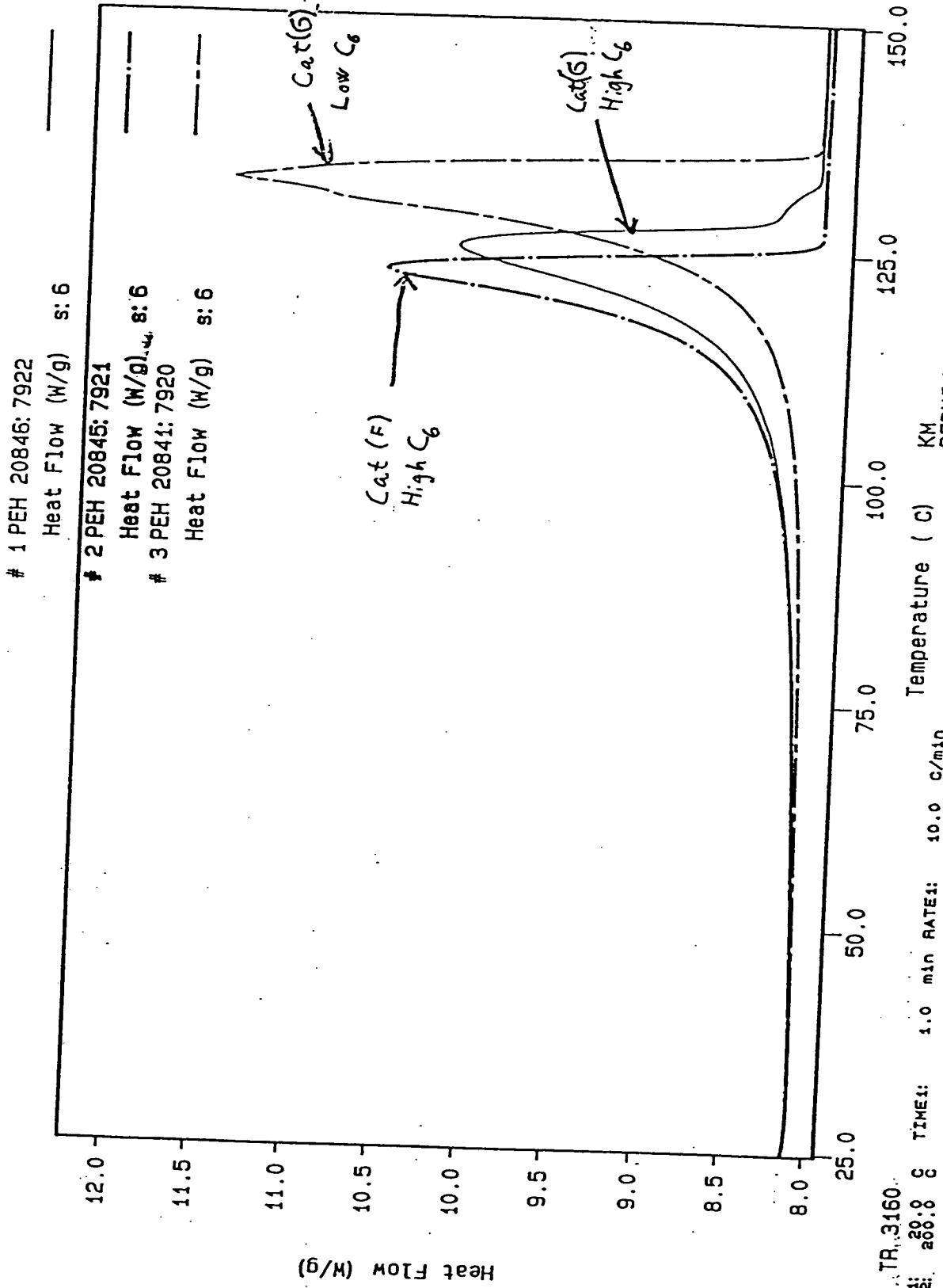
Figure 7

Curv 1: DSC

File Info: 7922

Sample Weight: 6.300 mg

PEH 20846



PG CB 000270

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